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EMITTED FROM A COAL-FIRED POWER PLANT

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ATMOSPHERIC BEHAVIOR OF TRACE ELEMENTS ON PARTICLES  
EMITTED FROM A COAL-FIRED POWER PLANT

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Abstract--Filter and cascade impactor samples of suspended particles were collected in-stack and at distances up to 64 km downwind in the plume of a large western coal-fired power plant to investigate modifications of distributions of minor and trace elements among particle sizes during transport. Samples were analyzed for 40 elements by instrumental neutron activation analysis. Precipitator malfunction during the experiment caused greater than normal emission of large particles, and concentrations of As, Zn, Sb, Mo, Ga, W, U, V and Ba in plume particulate material were enriched relative to their concentrations in stack particles by factors of 1.5 to 3.0, primarily because of sedimentation of these large particles. Selenium was enriched by up to 7-fold (plume:stack) due in part to vapor deposition. Enrichment of elements in the plume relative to more typical in-stack particles were  $\leq 20\%$  for all elements except Se, which was enriched 2.5-fold. Coagulation of particles in the plume leads to preferential decrease in concentrations of the above elements in the submicrometer particle size range. Concentrations of Se on particles in the stack and plume

suggest that most of the Se vapor in stack gases condensed on particles soon after emission. Source signatures measured for Se must account for vapor deposition. While some post-emission modifications of elemental signatures of particles may occur for poorly controlled plants, little change is expected for well controlled plants. Bimodal size distributions of particles emitted from pulverized coal combustion are preserved during atmospheric transport up to 64 km.

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## INTRODUCTION

There are two fundamentally different approaches to source apportionment: the classical technique involving the coupling of source-emissions inventories with dispersion models and the newer, receptor-based techniques, which depend on detailed ambient and source composition data. Use of the latter is rapidly expanding (Hopke, 1985), especially the application of hybrid receptor models, which attempt to allocate secondary particulate matter (Lewis and Stevens, 1985). For receptor modeling to be successful, extensive source-composition data are required. Several studies of particulate emissions from coal-fired power plants have been reported (Davison et al., 1974; Kaakinen et al., 1975; Klein et al., 1975; Gladney et al., 1976; Block and Dams, 1967; and Ondov et al.,

1979a,b). Concentrations of many elements are enriched inversely with particle size by deposition of vapor-phase components and through preferential penetration of fine particles through emission-control devices. Several of these "enriched" elements are useful as tracers of coal combustion, especially Se (Andren et al., 1975; Germani, 1980), and possibly B (Fogg and Rahn, 1984). Effects of emission-control strategies, coal chemistry, and plant operation on compositions of particles emitted from power plants, however, are not well-known and much additional data are needed for use in receptor models.

An assumption common to receptor models is that compositions of particles, as determined in stacks, remain unchanged after atmospheric discharge. Yet few elemental measurements have been made on particles collected in plumes of coal-fired plants. Particle coagulation, sedimentation, and condensation or adsorption of gaseous species may change chemical and physical characteristics of stack-emitted particles during transport downwind. Boron, Hg, Se and, sometimes, Br and I are enriched in stack particles and all have significant vapor-phase components at stack-gas temperatures (Germani, 1980; Fogg and Rahn, 1984; Andren et al., 1975). Clearly, atmospheric behaviors of their vapor-phase components must be understood before they can be properly used in receptor models.

We have compared elemental compositions of particles in the plume with those of particles collected in-stack at a coal-fired power plant. The plant was a large western facility with five

coal-burning generators, each burning the same low sulfur (0.5%), high ash (22%) pulverized western coal. Two nearly identical units (each 653 kg/s steam capacity) were equipped with coldside electrostatic precipitators with rated particle-removal efficiencies of 97%. Three smaller units (two 160 and one 203 kg/s steam capacity) were equipped with high-energy Venturi scrubbers with rated efficiencies of 99.2%. Owing to the smaller capacity and lower stack heights of the scrubber-equipped units, and large differences in efficiencies between the ESP- and scrubber-equipped units during our study, the near-plume samples primarily represented the ESP-equipped units. Other details of the units tested are described by Ondov et al. (1979a,b).

#### SAMPLE COLLECTION AND ANALYSIS

Particulate samples were collected on filters along the plume axis at 0-8, 8-16, and 32-64 km from the plant on February 18th, 1976 and in impactors at 8-16, 16-32 and 64-121 km on the 19th, using the National Center for Atmospheric Research's (NCAR's) twin-engine Beechcraft. Fourth and fifth impactor samples were collected on the 13th at 0-8 km in the plume, and at 32-64 km upwind to evaluate background particles. Filter samples were collected isokinetically at 1 cfm on 100-mm diam, 0.4- $\mu$ m-pore Nuclepore filters using an exterior sampling probe. The same probe was alternately used to collect impactor samples with the MRI Model 1502 cascade impactor, also operated isokinetically at 1 cfm. The aircraft was equipped with a condensation nucleus counter and a continuous SO<sub>2</sub> monitor to aid in plume tracking. Polycarbonate

impactor substrates were coated with Apiezon vacuum grease. Air speed during sampling was 260 km/h. During each plume sampling episode, sampling was done within the readily visible plumes of the ESP-equipped units. Near the stacks, the scrubber plumes were readily identified by steam and observed to be located below the ESP plumes. However, the plumes probably mixed at the greater distances.

Five filter and 5 MRI impactor samples were collected during 6 sampling episodes, each lasting up to 7 h. Plume sampling usually began at dawn to take advantage of early morning inversions during which the plume was well defined. Sampling times were typically 60 min for samples collected within 32 km of the plant and 120 min for the 32-64 km samples. Background samples were collected for 120 min at 32-64 km upwind from the plant. Meteorological conditions were characterized by an early morning, ground-based diurnal inversion on each sampling episode. During these periods, a cold-air drainage flow generally followed along the area's sloping river basin, resulting in an easterly wind with a northerly component. During the afternoon, after break-up of the morning inversion, the mean transport vector was generally from the northwest. Because of this reciprocating weather pattern, background samples may have been influenced by aged plume aerosol. Winds at plume height were typically 4.5 m/s.

Impactor and filter samples were also collected in-stack at one ESP-equipped unit (Unit 4), and at the outlet of the mist eliminator of a scrubber unit (Unit 1) using 7-stage University

of Washington Mark-3D Source Test cascade impactors, and 0.4- $\mu$ m Nuclepore filters as part of a 10-d sampling program to compare emissions from the scrubber- and ESP-equipped units (Ondov et al., 1979b). Two impactor and 3 filter samples were collected from both Units 1 and 4 concurrently with plume samples on both the 18th and 19th of February. Stack samples were collected with an EPA sampling train modified to permit in-stack operation of the collectors as previously described (Ondov et al., 1979b). Stack-sampling parameters are listed in Table 1. Ambient temperature and pressure were 10°C and 837 mb.

On both the 18th and 19th, several precipitator sections were inoperative on both Units 4 and 5, causing considerably reduced particulate removal efficiencies. Unit 2 was operated at ~60% load on both days. Unit 3 operated at ~80% load on the 18th and was down on the 19th, and Units 4 and 5 were operated at reduced load on the 19th. Generating loads and particulate emissions for the five units are listed in Table 2. Because particulate emissions differed so much from day-to-day, only plume and stack samples collected in the same periods may be compared.

Samples were analyzed for up to 43 elements by instrumental neutron activation analysis techniques previously described (Heft, 1977). Analyses of coal were reported by Ondov et al. (1979a,b). Analyses were verified by comparing results of parallel analyses of National Bureau of Standard's reference materials SRM 1632, coal, and SRM 1633, coal fly ash, with interlaboratory analyses of SRMs and size-fractionated fly ash samples (Ondov et al., 1975;



ibid., 1976). Size distributions of particles collected on several impactor stages, backup filters and total filters were measured by scanning electron microscopy as described by Ondov et al. (1978).

## RESULTS AND DISCUSSION

Results for stack- and plume-filter samples are listed in Tables 3 and 4, respectively, and those for impactor samples in Table 5 and Figs. 1-3. Much of the stack data were reported previously as part of a comparison of elemental emissions and particle size distributions from the scrubber-equipped unit in February with those from the ESP-equipped unit the previous July (Ondov et al., 1979b). In the present experiment, emission characteristics of the ESP-equipped unit (i.e., February data, not previously reported) were qualitatively similar to those previously reported for that unit in July. Briefly, particles collected from each unit were distributed bimodally, reflecting a distinct submicrometer distribution mode, due in part to condensation aerosol, and a larger mode, resulting from penetration of residual mineral matter through the control devices. The distinct distribution of submicrometer particles is readily observed in classified data obtained by electron microscopy. However, the submicrometer mode appears only as an increase in mass collected on the back-up filter because the particles in this mode were too small to classify with the impactors used. Distribution parameters (i.e., mass median aerodynamic diameter, MMAD, and geometric standard deviation,  $\sigma_g$ ) of the larger mode depend strongly on the efficiency of the emission-

control systems. A third mode (8.0  $\mu\text{m}$ ) was often observed among scrubber-emitted particles and is attributed to liquid aerosol from the mist eliminators. In general, particle-size distributions of most trace elements observed in the ESP and scrubber aerosols were similar to those of either Se or Al, shown in Fig. 1. Bimodal distributions obtained by particle counting with electron microscopy showing both modes were published previously (Ragaini and Ondov, 1977).

During plume-sampling episodes, both ESP-equipped units suffered failures of some precipitator sections, and Unit 5 also suffered boiler upsets. Distribution parameters of stack particles collected from Unit 4 on February 19th are listed in Table 6. On this date, precipitator efficiency was estimated to be <85% and MMADs of particles bearing various elements in the stack were up to twice those observed from the same unit during the previous July (Ondov et al., 1979a,b). The MMADs for elements measured, however, were about the same for each of the precipitator configurations experienced on February 18th and 19th, despite the factor of 1.8 difference in particulate emission rates. Median values of MMADs of the elements in particles from the scrubber unit ranged from 0.49 to 7.7  $\mu\text{m}$  (ibid., 1979b).

As indicated above, plume samples were collected within the the higher, more visible plume of the two ESP-equipped units. However, despite the differences in the effective plume heights [449 and 180 m, respectively, for ESP- and scrubber-equipped units, estimated from Holland's equation (Turner, 1970)], the plumes

probably mixed at some distance downwind, making plume samples a composite of materials from the two kinds of units. Under normal operating conditions, combined particulate emissions of the two ESP-equipped units are more than 30 times greater than those of the three scrubbers. But due to differences in removal efficiency-vs-particle size characteristics for the two types of control devices (see Ondov, 1979b), the submicrometer particulate emissions of some elements (e.g., Sb) are typically greater from the scrubber-equipped units than from the ESP units.

During our study, particulate emissions from the ESP-equipped units exceeded those of the scrubber-equipped units by 80 to 600 times (see Table 2). To estimate maximum possible contributions of the scrubber-equipped units to concentrations of elements measured in plume samples, we computed emission rates (g/s) of minor and trace elements from the scrubber- and ESP-equipped units that were sampled and estimated elemental emission rates for the other units using the trace element concentrations measured for Units 1 and 4, and coal-feed rates and estimates of the particulate control efficiencies for the other units. Elemental emission rates for Units 1 and 4 were computed using concentrations listed in Table 3, measured stack-gas velocities, and stack diameters. Ratios of the emission estimates for scrubber units to total plant emission rates for several elements are listed in Table 7 for February 18th and 19th. The scrubber units accounted for <15% of total plant emissions for any element, including Se, for which the largest contribution might have occurred. Thus, even if plumes from the

various units did mix, scrubber emissions would not have affected concentrations of most elements observed in near-plume samples.

As indicated in Table 6, MMADs of most elements in plumes were less than those in the ESP stack, and further decreased in successive plume samples, presumably as a result of large-particle sedimentation. As particulate emissions from the scrubber-equipped units contained far fewer settleable particles, their contribution to the plant's plume undoubtedly increased with distance from the plant and, as noted below, the impact of scrubber emissions on the more distant plume samples was apparently observed for some elements.

As indicated in Table 4, elemental concentrations ( $\mu\text{g}/\text{m}^3$ ) successively decreased by a factor of 5 between samples collected at the 0-8, 8-16 and 32-64 km distances. Because of large particle sedimentation and the uncertainty in total plant emissions, dilution between plume and stack samples could not be determined accurately. To avoid dilution effects, we computed enrichment factors (EF) for elements on plume particles relative to those observed in the stack. Normalization of the plume data to those measured for ESP-equipped Unit 4 was chosen in view of the overwhelmingly large emission rates of the ESP-equipped units and because they are identical units that burned the same coal. The EFs are defined for each element (X) as follows:

$$EF = [X]/[Al]_{\text{plume}}/[X]/[Al]_{\text{stack}},$$

where the numerator is the ratio of concentrations of other elements in the plume to that of Al, and the denominator is the analo-

gous ratio for elements in stack aerosol. The EFs for plume filter samples are listed in Table 8. Results of plume impactor samples were similarly normalized, but to elemental concentrations in the feed coal, so that the various plume and stack distributions could be viewed separately on the same graph. The resulting EFs are plotted vs. particle diameter in Figs. 2 to 5 for selected elements.

As indicated in Table 8, many elements that usually occur in nonvolatile compounds, including Na, K, Ca, Sc and lanthanides, show no enrichment with respect to Al in stack particles, nor do their EFs vary with distance from the stack, except for a slight decrease in the EFs of several elements in the 32-64 km sample. We refer to these elements as "Group 1." Most elements in Group 2, i.e., Mo, V, Ba, U, Ga, In, As, W and Se, have much larger fractions of their mass on fine particles than does Al, and are enriched in the plume relative to the stack by factors ranging from 1.6 to 7, the latter for Se. These elements typically show an inverse relationship between concentration and particle size. Most of the EFs are  $<3$ , and no further change in enrichments is observed with increasing distance from the plant, except for a slight decrease in EF in the 32-64 km sample. As discussed above, MMADs for nearly all elements decrease with distance from the plant, presumably as a result of sedimentation of the larger particles (see Table 6). Thus, for most elements in Group 2, the enrichments in plume particles relative to stack particles may be attributed to the preferential removal of large, relatively unenriched

particles, which apparently occurred within a few hundred meters of the stack. The slight decrease in EFs observed for Group 2 elements in the 32-64 km sample might reflect the influence of another source, possibly wind-blown soil, which would elevate the Al concentration.

In this experiment, MMADs for particles emitted from the ESP-equipped unit were about twice those observed the previous July when the ESP was operating at its normal (97%) efficiency (Ondov et al., 1979a,b). For comparison, EFs for plume particles were computed relative to the July Unit-4 data and are also listed in Table 8. Except for Se and possibly Ga, no Group-2 elements are significantly enriched relative to the July stack particles, indicating that an initial enrichment in the near-plume is probably important only for poorly controlled plants that emit large amounts of large settleable particles. Below, the net enrichment for Se in the plume relative to the July data is attributed to vapor condensation.

Except for Fe, EF-vs.-particle-size curves for Group-2 elements are similar to those shown for As and Sb in Figs. 2 and 3. These figures show EF-size curves for particles collected in the stack of the ESP-equipped unit and in the plume at 8-16 and 16-32 km. Note that EFs for fine particle fractions (i.e., those with diam  $< 2 \mu\text{m}$ ) clearly decrease with distance from the plant, while EFs for larger particles remain about the same. This decrease in EF for fine particles appears to result from intermodal particle coagulation for an aerosol, in which particles are enriched inverse-

ly with respect to size. The rate of coagulation between particles increases as the difference in their size increases. Therefore, a decrease in the small-particle EF would result from preferential removal of the smallest, most highly enriched particles present in each of the fine-particle fractions collected in the impactor, by larger particles which may ultimately settle. The EF for the large particle fractions wouldn't change because the mass of enriched material transferred is small relative to that already present in the large particles.

As suggested above, the influence of the scrubber plumes probably increased with distance from the plant due to preferential sedimentation of ESP particles and increased mixing as the plumes dispersed. Therefore, one might think that the decrease in fine particle EFs for Group-2 elements resulted from increased scrubber influence. However, EFs of Group-2 elements relative to Al in fine scrubber particles were about the same or greater than those in fine ESP particles (see Table 5). Thus, increased scrubber influence could not have caused the observed decrease in the fine-particle EFs.

Enrichment factors for Sb, Zn, and Co (Group 3 in Table 8) were about equal to those of the Group-2 elements in the near-plume (i.e., 0-8 km) sample, but increased with distance. Potassium is included in Group 3, as its EF may have increased slightly with distance, but given the large uncertainties (see Table 8), K could easily be included in Group 2 or Group 1. Chromium was highly enriched in the 8-16 km sample, but was measured in only that one

sample. Bromine was highly enriched over ESP particles in the near-plume sample and its EF increased dramatically with distance. The near-plume increase in the EF for Br could arise for any of several reasons, including large particle sedimentation, and condensation of gaseous Br. As indicated in Table 9, the concentration of Br in background particles and its EF (relative to crustal material) were both greater than those in the plume particles. Therefore, the increase in EF for Br with distance is clearly the result of the plume mixing with background aerosol. Concentrations and EFs for Co, Zn, Sb and Cr were greater than those in the background sample collected upwind of the plant. Thus, increases in EFs for Co, Zn and Sb could not have been caused by mixing with the background air sampled, although they might be the result of an interfering source. We suspect, however, that increases in EFs with distance resulted from mixing of the scrubber and ESP plumes as they continued to disperse.

As shown in Table 5, Group-2 and -3 elements were more highly enriched in scrubber particles than in ESP particles. Chromium, for example (see also Fig. 4), was uniformly enriched in plume particles of all sizes relative to particles from the ESP-equipped unit. Furthermore, the EF for Cr in fine particles increased slightly between the 8-16 and 16-32 km samples. An increase in fine particle EFs in successive plume samples was more pronounced for Mn (Fig. 5) and also observed for Co. Enrichments for Mn and Cr in large scrubber particles (Table 5, Figs. 4 and 5) were much higher than those in ESP particles. In these and previous



experiments, we observed that scrubber aerosol contained large numbers of highly acidic water droplets ranging in size from about 2 to 30  $\mu\text{m}$  (Ondov et al., 1979b). These invariably contained large amounts of Co, Cr, Mn and Zn, especially the 8- $\mu\text{m}$  particles, probably as a result of leaching of internal metal surfaces (Table 5), possibly within the recycle loop. Elements scrubbed from the gas phase (e.g., Se) are also enriched in these droplets, as are most Group-2 elements such as Sb, and Mo, which are enriched on fine particles. Some of these highly-enriched fine particles are probably captured by the droplets, thereby enriching the droplets. Also, we suspect that leaching of some soluble elements from fly ash particles occurs in the recycle loop, thereby enriching the liquor and, hence, the droplets. When the water evaporates, highly enriched submicrometer particles are formed. We attribute the increases in EFs for Group-3 elements observed for the second and third filter (i.e., 8-16 and 16-32  $\mu\text{m}$ ) samples to increased mixing of the plumes with distance. The increase in fine-particle EFs is probably augmented by formation of new, highly enriched submicrometer particles by droplet evaporation either in-stack downstream of our sampling port or in the plume. The small enrichments of Group-3 elements (except Br) in the near-plume sample are consistent with our view that this sample was not appreciably influenced by the scrubber-equipped units. Enrichment factors for elements with low abundances in the particles are affected most. Thus, EFs for Fe (about 3% by weight in fly ash), Na and Ca (Group 1 elements), for example, are little affected by the scrubber contri-

bution (see Table 5).

Selenium and Br have large vapor-phase components at stack-gas temperatures and could condense on particles at the lower plume temperatures (Andren et al., 1975; Germani, 1980). To investigate the impact of vapor deposition of these and other elements on the near-plume samples, we constructed a mass balance for the coal and various ash streams using data listed in Table 10. The total ash produced in the boiler was estimated from the coal-feed rate and its ash content. The ESP efficiency selected was consistent with the measured stack emission rate and estimated rates of ash production and bottom-ash removal. The coal-feed rate was calculated from the gross generating load, energy-conversion efficiency and heat content of the coal. Elemental fluxes in the various streams were computed from average concentrations of elements in each stream and the mass-flow rates listed in Table 10. Elemental fluxes in stack particulate emissions were computed from their measured stack-gas concentrations ( $\mu\text{g}/\text{m}^3$ ) using the measured volumetric flow rate. The coal-feed rate was adjusted by a factor of 1.036 (to yield 108,410 g/s) to achieve a perfect mass balance for Al.

A negative mass balance indicates a vapor component. Uncertainties in each stream and in the elemental analyses were propagated through the mass balance, the minimum uncertainty being estimated as 15% for Al. Deviations for most elements were  $< \pm 5$  or 6%, so no vapor-phase component could be detected. Only Se and Br had significant deviations. More than 59% of the Br and about 21% of the Se

introduced in the coal were emitted in the gas phase. The Se vapor flux is about 40 mg/s, corresponding to ~39% of total Se entering the plant (column 2 of Table 10) and ~64% of the stack-emitted particulate Se (i.e., 64% of  $54.7 \pm 2.5 \mu\text{g}/\text{m}^3$  from Table 3) or  $35 \pm 23 \mu\text{g}/\text{m}^3$ . Given the uncertainty of  $\pm 14\%$  in the Se mass balance, the Se vapor concentration ranges from 12 to  $58 \mu\text{g}/\text{m}^3$ .

Billings et al. (1973) suggest that Se vapor in stack gases of coal-fired power plants exists in the elemental state. From thermodynamic data reported by Pankratz (1978), the equilibrium vapor concentration of Se metal (including  $\text{Se}_2$ ,  $\text{Se}_3$  and  $\text{Se}_6$ ) at the stack temperature ( $110^\circ\text{C}$ ) of the ESP unit would be  $\sim 13.3 \mu\text{g}/\text{m}^3$ . This agrees well with the lower estimate of the Se vapor concentration of 12 to  $58 \mu\text{g}/\text{m}^3$  obtained from the mass balance, suggesting that the stack gas may have been saturated with Se vapor. Both estimates are so uncertain that it is impossible to be certain that the gas is saturated based on these studies alone.

Condensible Se vapor is clearly present, as glass probes used in stacks often collect visible (red) deposits of Se, and as evidenced by the low apparent collection of particulate Se by the Venturi wet scrubber (VWS). Based on concentrations of Se on particles at the inlet and outlet of the VWS, for example, Se is collected with an apparent efficiency of only about 55%, whereas, for other fine-particle elements such as As and Sb, the apparent collection efficiency is about 90%. (Elements associated with larger particles are collected with efficiencies  $>90\%$ .) This low apparent collection efficiency for Se is attributed to Se vapor condensation as the

gas is cooled from  $-130^{\circ}\text{C}$  at the inlet to  $54^{\circ}\text{C}$  at the outlet. Using the ratio of Sb (whose vapor component is assumed negligible) in the plume and stack particles (Feb. 18 data), the dilution factor for the 0-8 km sample is estimated to be 1026. Division of the estimated vapor component by 1026 yields  $0.034\text{ }\mu\text{g}/\text{m}^3$ , which is about 6000 times the predicted equilibrium concentration ( $0.0059\text{ }\mu\text{g}/\text{m}^3$ ) at the plume temperature ( $10^{\circ}\text{C}$ ). According to this calculation, most Se present as vapor in the stack should condense on particles in the plume to yield a particulate Se concentration in the range from 0.065 to  $0.11\text{ }\mu\text{g}/\text{m}^3$ . This range is in excellent agreement with the value of  $0.105\text{ }\mu\text{g}/\text{m}^3$  observed in the near-plume sample. As the EF for Se did not change in successive plume samples, no additional Se appears to have condensed.

As indicated in Table 8, the plume EFs for Se were greater than those of other Group-2 elements. By contrast with other elements in Group 2, Se was significantly enriched relative to the July stack data. The enrichment of Se in the plume results from two near-plume processes: the settling of Al-rich, Se-deficient particles and deposition of Se vapor. Normalization of the plume data to the July stack data effectively removes the effect of large particle sedimentation on the EFs, reducing them and the EF for Se, the latter becoming  $\sim 2.5$ . However, this does not account for the fact that, under normal circumstances, there would be less particulate material in the plume and, thus, a smaller Al concentration in the denominator of  $(\text{X}/\text{Al})_{\text{plume}}$  in the EF equation. The emission of Al in July was a factor of 6.1 less than in Febru-

ary. Thus, the Al concentration for plume particles should be reduced by this factor. Also, particulate Se penetrates the ESP more efficiently than does Al because of differences in their size distributions. Particulate Se emission experienced only a 2.2-fold reduction; however, we assume that the gas-phase Se would be released at the same rate as it was during our experiment. The net concentration of particulate Se in the plume, which contains both primary and secondary contributions, however, is reduced considerably less, i.e., by only about 53 to 64% depending on whether we use the equilibrium Se vapor concentration or the value calculated from the mass balance. Thus, accounting for all of these factors, the final EF for plume Se with respect to stack Se becomes 2.5 (from Table 8) times  $6.1 \times (0.53 \text{ or } 0.64)$ , i.e., about 8.1 or 9.8. Receptor modelers typically have used only stack data, but the EF for Se appropriate for receptor-model calculations is probably much greater than the value determined from stack measurements. For plants similar to the ESP-equipped unit (i.e., similar efficiency) studied here, the increase would be a factor of 8 to 10.

Wangen (1981) collected plume-particulate samples with a cascade impactor from June, 1977 through January, 1978 at a ground-level station located 8-km west of the same plant during fumigation episodes. Comparisons with our data are at best tenuous, as plant operating conditions may have differed (and were not monitored) in his study, and no coal samples were collected. However, as previously reported (Ondov et al., 1979a), the composition of the coal

burned by this plant was remarkably constant between June, 1975 and February, 1976. During this period, for example, the Se concentration in coal varied by only about 12%. Thus, the coal and the EFs for elements in ESP plume particles might be expected to have remained constant through Wangen's study. To compare his data with ours, we normalized Wangen's data by computing EFs relative to stack particles collected in July as described above and listed the results in Table B. Except for Se, Wangen's Group-2 elements are deficient with respect to their concentrations in July stack particles; or, alternatively, Al is enriched in his samples. This might be the result of insufficient background correction, differences in coal composition, or differences between his and our analyses. In Wangen's experiment, Se is enriched over our July stack aerosol by a factor of only 1.6, whereas we expect an EF of 8 to 10. Judging from the two- to three-fold deficiencies indicated for other Group-2 elements, an EF of from 3 to 5 might better represent the actual enrichment of Se to stack particles emitted during Wangen's study. As in our study, Cr is highly enriched in Wangen's ground-plume study, and Co and Zn may also be slightly enriched. The small enrichments for La and Sc (Group 1) are probably not significant.

#### CONCLUSIONS

In these experiments, in which the particulate control systems operated at reduced efficiencies, size distributions and enrichment factors for trace elements appear to have been modified by sedimentation and kinematic coagulation between the fine and large, settle-

able particles. From the standpoint of receptor modeling, the overall changes in EFs for "enriched" elements resulting from these processes, ranging from 1.35 for Fe to about 3 for Sb, were quite large, and may be important for poorly controlled plants. However, differences between EFs for plume and stack particles were negligible when the ESP operated normally and removed most readily settleable particles and are not expected to be significant for well-controlled, modern plants. Exceptions are Se and possibly Br, for which condensible vapor components are considerable. Relative to the February ESP data, Se was enriched in plume particles by about a factor of 7, in part because of the settling of Se-deficient, Al-rich particles, and in part due to the condensation of Se vapor on particles in the cooler plume. Our attempts to account for the elevated emission rates and presence of the readily settleable particles suggest that Se is probably enriched by a factor of between 8 and 10 in the plume of the plant studied during normal operating conditions. While similar enrichments might be expected in plumes of other well-controlled pulverized coal-fired power plants, the concentration of Se in coal, plant design, and operational characteristics (especially flue-gas temperature and placement of the particulate control device) will affect the EF for Se in plume particles. Because of its value as a tracer of utility coal combustion emissions, the atmospheric behavior of Se warrants greater attention.

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**Table 1. Stack-sampling parameters.**

	Unit		
	VWS <sup>a</sup> 1,2	VWS <sup>a</sup> 3	ESP <sup>b</sup> 4,5
Height, m	76.2	76.2	91
Outlet ID, m	5.36	4.37	8.69
Gas Velocity, m/s	28.0	37	28.0
Gas Temperature, °C	54	54	110
Effective Plume Height, <sup>c</sup> m	180	178	463

<sup>a</sup>Venturi wet scrubber-equipped unit.

<sup>b</sup>Electrostatic precipitator-equipped unit.

<sup>c</sup>Calculated via Holland's plume-rise equation (Turner, 1970).

Table 2. Particulate emission rates for five coal-burning units, kg/s

Unit	Actual Power Level, MW		Emission Control Device	Emission Rate	
	2/18	2/19		2/18	2/19
1	186	187	VWS <sup>a</sup>	4.7 <sup>c</sup>	5.6 <sup>c</sup>
2	116	115	VWS <sup>a</sup>	2.9	3.4
3	191	d	VWS <sup>a</sup>	4.8	— <sup>d</sup>
4	762	615	ESP <sup>b</sup>	4.8x10 <sup>3c</sup>	1.7x10 <sup>3c</sup>
5	760	727	ESP <sup>b</sup>	2.6x10 <sup>3</sup>	1.75x10 <sup>3</sup>

<sup>a</sup>Venturi wet scrubber.

<sup>b</sup>Electrostatic precipitator.

<sup>c</sup>Measured values. All others estimated from engineering parameters.

<sup>d</sup>Unit not operating.

Table 3. Concentrations of particle-borne elements in stack gases of two coal-burning units at a western power plant,  $\mu\text{g}/\text{m}^3$

Element	Unit 1 <sup>a</sup>		Unit 4 <sup>a</sup>	
	2/18 <sup>b</sup>	2/19	2/18 <sup>b</sup>	2/19 <sup>c</sup>
Al	1290+150	1050+160	404000+36000	252000+23000
As	10.9+1.3	11.0+0.8	118+7	59.0+6.0
Ba	336+35	193+17	5870+350	4920+590
Br	1.9+0.2	1.8+0.8	---	---
Ca	1604+200	1890+80	69900+7300	56500+2100
Ce	1.0+0.2	0.92+0.06	380+20	235+18
Cl	68+14	160+10(1)	---	310+230(1)
Co	0.73+0.74	1.0+0.9	42.8+2.9	25.7+2.1
Cr	55+72	82+65	126+18	156+19
Cs	---	---	10.8+0.5	6.11+0.34
Cu	39+20	---	---	---
Fe	640+360	715+340	87800+5100	53400+3400
Ga	4.7+0.2	3.6+0.3	250+14	148+12
In	0.0285+0.0060	0.019+0.0013	1.24+0.04	0.81+0.12
K	34+12	53+17	22800+2000	14000+1600
La	0.52+0.11	0.48+0.05	210+12	132+13
Mg	190+60	550+270(1)	36000+12000	26000+4000
Mo	4.1+0.9	4.7+1.1	66.4+6.7	37.2+4.6
Mn	130+170	120+90	959+60	592+40
Na	310+130	360+140	40400+2900	25800+3100
Ni	13+2(1)	44+28	---	95+32
Rb	---	---	163+15	96.3+9.4
Sb	2.6+0.3	2.6+0.35	19.5+1.0	10.4+0.8
Sc	0.112+0.008	0.103+0.008	46.0+2.7	27.4+2.3
Se	19.7+5.5	27.3+2.5	54.7+2.5(1)	46.3+6.1
Sm	0.070+0.010	0.048+0.012	28.3+1.7	17.8+2.4
Sr	17+2(1)	20+2	1320+14	815+96
Ta	0.067+0.007(1)	0.046+0.008(1)	7.73+0.46	4.9+0.5
Th	0.20+0.02	0.20+0.01	86.5+7.0	53.8+4.9
Ti	88+12(1)	61+24(1)	17500+1800	11100+1200
U	0.95+0.25	0.93+0.29	41.9+3.0	26.2+ 3.2
V	20.4+2.6	15.2+1.9	497+23	299+15
W	2.0+0.2	2.0+0.2	23.2+2.9	14.8+2.0
Zn	18+5	58+68	507+37	263+15
Zr	8.2+3.0(1)	---	788+18	539+69

<sup>a</sup>Uncertainties reflect only those from counting statistics of samples and blanks.

<sup>b</sup>Average and standard deviation of 4 filter and cascade impactor samples unless indicated by number in parentheses.

<sup>c</sup>Average and standard deviation of 3 filter samples unless indicated.

Table 4. Concentrations of elements borne by particles in a power-plant plume,  $\mu\text{g}/\text{m}^3$ .

Element	Data of February 18, 1975		
	0-8 Km	8-16 Km	32-64 Km
Al	110+4	26.5+0.6	4.3+0.7
As	0.087+0.003	0.017+0.0015	0.0031+0.0005
Ba	2.87+0.07	0.57+0.03	0.106+0.009
Br	0.063+0.008	0.048+0.005	0.032+0.003
Ca	---	6.9+1.6	---
Ce	0.11+0.015	0.021+0.003	0.0042+0.0007
Co	0.035+0.002	0.0070+0.0010	0.0034+0.0002
Cr	---	0.41+0.11	---
Cu	---	1.1+0.2	---
Eu	0.00117+0.00009	0.00023+0.00004	0.000041+0.000012
Fe	32.2+1.9	6.4+0.2	1.25+0.09
Ga	0.144+0.009	0.026+0.005	0.0048+0.0016
Hf	0.0125+0.0015	0.0022+0.0002	0.00034+0.00006
I	---	0.016+0.002	0.0092+0.002
In	0.00090+0.00011	0.00015+0.00002	---
K	8.1+0.9	2.8+0.6	0.53+0.21
La	0.063+0.0015	0.0117+0.0007	0.0018+0.0002
Mg	8.3+3.6	2.4+0.8	---
Mo	0.031+0.010	---	---
Mn	0.322+0.005	0.078+0.003	0.011+0.0015
Na	11.9+1.4	3.7+1.1	<1.4
Ni	1.1+0.3	0.19+0.06	0.23+0.02
Sb	0.019+0.0013	0.0081+0.0003	0.00463+0.00013
Sc	0.0149+0.0004	0.00281+0.00006	0.00041+0.00002
Se	0.105+0.009	0.0201+0.0014	0.0033+0.0005
Sm	0.0089+0.0005	0.00160+0.00008	0.00027+0.00002
Ta	0.0047+0.0017	0.00061+0.00013	---
Th	0.0026+0.0015	0.0055+0.0002	0.00079+0.00007
Ti	5.5+1.4	1.1+0.3	---
U	0.024+0.0014	0.0041+0.0003	0.00064+0.00012
V	0.22+0.03	0.044+0.006	---
W	0.019+0.003	0.0050+0.0011	---
Zn	0.38+0.09	0.24+0.04	0.089+0.018

Table 5. Enrichment factors vs particle size for VMS and ESP impactor samples collected on February 19th.

VMS	ESP	VMS	ESP	VMS	ESP	VMS	ESP	VMS	ESP	VMS	ESP	VMS	ESP
size, $\mu\text{m}$		Cr		Sb		Zn		Co		K		Br	
37	32	151.40	2.62	18.54	0.90	594.00	1.52	8.51	1.34	1.12	1.01	34.13	0.32
17.7	9.21	—	2.15	—	1.07	—	1.72	—	1.58	—	1.01	—	0.45
8.05	4.27	5190.00	2.35	32.95	3.12	40.20	3.98	133.75	2.92	—	1.02	129.45	—
3.45	3.03	558.50	3.82	16.10	4.23	7.61	6.38	22.30	4.44	—	1.11	60.55	0.24
1.69	1.82	345.00	4.53	16.35	5.36	13.08	5.72	15.95	2.96	0.79	1.19	40.45	2.85
0.93	1.08	292.50	3.77	20.25	5.99	23.47	6.33	9.55	2.73	1.17	0.94	36.35	0.87
0.48	0.615	31.65	8.54	41.00	8.49	12.82	5.63	2.24	2.61	0.67	0.80	40.40	2.52
0.2	0.2	227.00	224.95	199.00	72.05	25.15	8.14	15.14	3.68	0.43	0.54	76.80	18.90
multiplier <sup>b</sup>		0.000238		0.0000208		0.000556		0.0000705		0.0586		0.0000325	
size, $\mu\text{m}$		Mn		Fe		Mo		V		Ba		Na	
37	32	80.45	1.14	3.29	1.15	9.55	1.16	—	—	1.26	1.01	4.03	0.87
17.7	9.21	—	1.12	—	1.18	—	0.89	—	0.88	—	1.10	—	0.94
8.05	4.27	581.00	1.09	19.31	1.40	79.90	2.36	8.40	1.66	4.32	1.58	6.10	1.45
3.45	3.03	70.40	1.44	4.11	1.57	14.65	2.87	—	2.76	2.98	2.14	7.41	1.59
1.69	1.82	55.20	1.68	2.83	1.29	8.75	5.06	2.05	3.08	3.29	2.50	2.18	1.53
0.93	1.08	99.75	1.79	2.23	1.22	10.53	4.48	—	2.74	4.23	2.97	2.02	1.23
0.48	0.615	4.49	2.18	1.25	1.20	14.80	4.78	8.22	3.62	5.78	3.94	1.09	1.25
0.2	0.2	12.03	2.00	3.18	1.47	82.05	24.55	27.70	14.30	20.55	12.80	2.40	2.08
multiplier <sup>b</sup>		0.00204		0.219		0.0000905		0.000844		0.0142		0.0993	
size, $\mu\text{m}$		U		Ga		In		As		Se		La	
37	32	0.89	0.99	1.14	1.11	—	0.44	7.53	0.67	20.99	2.77	0.70	1.13
17.7	9.21	—	1.04	—	1.29	—	0.81	—	0.96	—	2.87	—	1.15
8.05	4.27	3.42	1.68	6.33	3.27	—	2.53	36.80	3.56	299.50	3.27	1.15	1.34
3.45	3.03	3.97	2.80	5.32	4.92	18.60	4.40	25.85	6.31	72.40	7.63	1.47	1.35
1.69	1.82	4.02	2.85	5.36	5.36	—	4.92	21.30	7.75	85.75	8.89	1.57	1.32
0.93	1.08	5.01	2.94	5.82	5.28	—	5.54	22.15	8.04	63.65	11.55	1.95	1.23
0.48	0.615	7.32	3.92	6.97	6.42	11.90	7.67	42.45	10.75	150.50	18.10	2.11	1.44
0.2	0.2	22.90	14.00	17.55	8.39	17.61	15.50	174.00	84.40	628.50	207.00	0.36	1.14
multiplier <sup>b</sup>		0.0000719		0.000288		0.00000132		0.0000963		0.0000590		0.000454	

<sup>a</sup>All data are averages of two impactor samples, unless one indicated.

<sup>b</sup>Data may be restored to  $\mu\text{g}/\text{m}^3$  by multiplying the EF by the multiplier for the element desired and again by the corresponding Al concentration ( $\mu\text{g}/\text{m}^3$ ) for the appropriate stage. Average Al concentrations ( $\mu\text{g}/\text{m}^3$ ) for stages 1-8 are respectively: 126, —, 31.3, 127, 80.5, 74.3, 659, 45.7 for VMS impactors; and 48000, 32800, 29200, 12600, 7560, 5610, 2060, 540, for the ESP impactors.

Table 6. Size distribution parameters of power-plant particles collected February 19th. Mass median aerodynamic diameter (MMAD),  $\mu\text{m}$ , and geometric standard deviation,  $\sigma_g$ .

Element	ESP (Unit 4)		Plume			
	MMAD <sup>a</sup>	$\sigma_g^a$	8-16 Km		16-32 Km	
	MMAD <sup>a</sup>	$\sigma_g^a$	MMAD <sup>a</sup>	$\sigma_g^a$	MMAD <sup>a</sup>	$\sigma_g^a$
Al	26	2.8	19	3.6	8.4	3.9
Sc	23	2.9	16	3.6	8.3	3.1
Na	20	3.0	15	3.3	2.4	6.7
Mn	22	3.2	8.8	4.8	3.6	6.5
Ca	--	--	22	2.7	~9	--
La	24	2.9	17	3.5	9.1	2.8
Fe	23	3.0	13	4.1	6.9	5.8
Mo	9.6	4.2	~4.5	5.2	--	--
Ba	13	4.1	10	4.3	5.4	4.0
U	14	3.0	10	4.4	8.4	2.1
Ga	12	3.3	8.2	3.5	6.7	3.0
Se	4.9	7.7	2.1	7.8	--	--
In	9.0	3.4	~10	2.8	7.8	3.1
V	8.8	3.6	13 <sup>b</sup>	4.1	8.5	2.5
As	6.0	4.6	5.2	4.2	3.9	4.0
W	5.9	4.6	6.1	4.7	6.1	1.8
Cr	9.5	7.0	0.6	4.2	1.0	8.0
Br	3.9	5.6	7.4	6.3	1.0	4.0
Sb	6.8	5.2	2.9	4.2	14	6.3
Zn	11	3.3	4.6 <sup>b</sup>	4.0	--	--
Co	16	3.2	7.7	4.4	3.9	7.3
K	25	2.9	16	4.1	--	--

<sup>a</sup>Median value of impactor samples collected on 19 February.

<sup>b</sup>The highest concentration was on 1st impactor stage. Individual MMAD values were computed nonparametricly.

Table 7. Contributions of elements emitted from wet scrubber units to the total plant emission, %.

Elements	<u>February 18</u>	%	Elements	<u>February 19</u>	%
Al, Sc, Na, K, T: Sr, lanthanides, Fe, Ca, Ga, In, U Zn, V, Ba, Mo, As W, Ni, Sb, Co		<u>≤ 5</u>	Al, Sc, Na, K, Ti Sr, lanthanides Fe, Ba, Ca, Ga, In, U, Co, V, W, Mo, As,		<u>≤ 5</u>
Br, Se		8.5, 14	Sr, Br, Se		6-12
Cr		1.6-11	Cr		3.0-19
Mn		0.2-13	Mn		1.2-8.2

Table 8: Enrichment of elements on particles collected on filters in the plume relative to stack aerosols of a coal-fired power plant.

Element	Enrichment Factor					
	Relative to February stack data			Relative to July Stack Data		
	0-8 km	8-16 km	32-64 km	This work, 8 km	Wangen et al., 8 km	
				625 MW	515-530 MW	625 MW
Group 1						
Al	$\approx 1.0$	$\approx 1.0$	$\approx 1.0$	$\approx 1.0$	$\approx 1.0$	$\approx 1.0$
Sc	$1.2 \pm 0.3$	$1.1 \pm 0.2$	$0.8 \pm 0.2$	1.0	0.98	1.2
Na	$1.1 \pm 0.3$	$1.7 \pm 0.6$	$0.7 \pm 1.2$	0.74	0.72	0.6
Mn	$1.2 \pm$	$1.5 \pm$	$1.1 \pm$	0.80	1.0	1.6
Ca	---	$1.8 \pm 0.6$	---	$1.4^b$	$1.5^b$	2.0
La	$1.1 \pm 0.3$	$1.1 \pm 0.1$	$0.9 \pm 0.1$	1.1	1.1	1.4
Group 2						
Fe	$1.35 \pm 0.2$	$1.4 \pm 0.2$	$1.3 \pm 0.2$	1.1	1.0	0.36
Mo	$1.7 \pm 1.2$	---	---			NR
V	$1.6 \pm 0.4$	$1.7 \pm 0.4$	---	0.71	0.79	0.48
Ba	$1.8 \pm 0.4$	$1.8 \pm 0.4$	$1.7 \pm 0.5$	0.51	0.74	0.36
U	$2.1 \pm 0.4$	$1.8 \pm 0.5$	$1.4 \pm 0.5$	0.91	1.2	0.28
Ga	$2.1 \pm 0.4$	$2.0 \pm 0.5$	$1.8 \pm 0.8$	1.1	1.2	0.43
In	$2.6 \pm 0.7$	$2.3 \pm 0.6$	---	1.25	1.7	0.71
As	$2.7 \pm 0.5$	$2.7 \pm 0.6$	$2.4 \pm 0.7$	0.78	1.05	0.37
W	$2.9 \pm 0.7$	$4.0 \pm 1.2$	---	0.87	1.1	0.29
Se	$7.0 \pm 3.2$	$6.9 \pm 3.1$	$5.6 \pm 2.9$	2.3	2.6	1.6
Group 3						
Cr	---	61+18	---	23	33	63
Br	40+20	$170 \pm 80$	$580 \pm 260$	130	---	0.85
Sb	$3.5 \pm 0.7$	$7.3 \pm 0.8$	$21 \pm 5$	1.2	1.5	0.51
Zn	$2.7 \pm 0.3$	$9 \pm 2$	$16 \pm 5$	1.1	1.5	1.4
Co	$2.9 \pm 0.6$	$3.0 \pm 0.8$	$7 \pm 2$	2.0	2.2	2.3
K	$1.3 \pm 0.2$	$2.3 \pm 0.6$	$2.2 \pm 1.0$	0.86	0.83	0.36

<sup>a</sup>Based on data reported by Ondov et al. (1978b). The enrichment factors of elements in plume (February data) and stack particles (July data) have been adjusted to account for the small difference in the concentrations of elements in coal that was burned during the two periods.

<sup>b</sup>Based on the 8-16 km sample of 18 February



Table 9. Comparison of plume and background particles for elements showing enrichment increasing with distance.

Element	Concentration ratio (plume:background) <sup>a</sup>		Enrichment factor relative to average crustal material <sup>b</sup>	
	0-8 Km	32-64 Km	32-64 Km <sup>c</sup>	background
As	26	0.9	33	~56
Br	<0.5	<0.25	250	~1100
Co	35	3.4	2.6	~1
Cr	---	41 <sup>d</sup>	16	~2
Zn	10	2.3	24	~13
Sb	50	12	440	~50
Mn	4.6	0.2	0.21	~2

<sup>a</sup>Based on filter samples collected in the plume on 18 February.

<sup>b</sup>Enrichment of plume and background aerosols computed relative to elemental concentrations in average crustal material as reported by Taylor (1964).

<sup>c</sup>Data based on filter sample collected at distance of 32 - 64 km on February 18.

<sup>d</sup>Value listed is for 8-16 km filter sample of February 18.

Table 10. Elemental flow rates in coal and fly ash streams of a 760 MW(e) utility generating unit, g/s.

Element	<u>Input</u>		<u>Output</u>		<u>Balance<sup>a</sup></u>
	Coal	Bottom	ESP	Stack	$\frac{[\Sigma \text{ash} - \text{Coal}]}{\text{Coal}} \times 100$
Total mass	108,410	5020 $\pm$ 1250	16414 $\pm$ 1260	3666 $\pm$ 730	0 <sup>b</sup>
Al	3200	620	2130	450	0 $\pm$ 15
Se	0.189	$\sim$ 0.005	0.065	0.062	-21 $\pm$ 14
Br	0.105 <sup>c</sup>	<0.01	<0.033	$\sim 3 \times 10^{-7}$	<-59

<sup>a</sup>Negative imbalance indicates possible vapor phase component.

<sup>b</sup>Based on coal of ash content of 23.15%.

<sup>c</sup>Datum based on analyses of coal collected in July 1976.

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### **Figure Captions**

- Figure 1. Emission rates of particulate Al and Se vs. particle size for ESP- and VWS-equipped coal utility boilers on the 18th of February.**
- Figure 2. Enrichment factor vs. particle size for As in stack and plume particles collected on the 19th of February.**
- Figure 3. Enrichment factor vs. particle size for Sb in stack and plume particles collected on the 19th of February.**
- Figure 4. Enrichment factor vs. particle size for Cr in stack and plume particles collected on the 19th of February.**
- Figure 5. Enrichment factor vs. particle size for Mn in stack and plume particles collected on the 19th of February.**

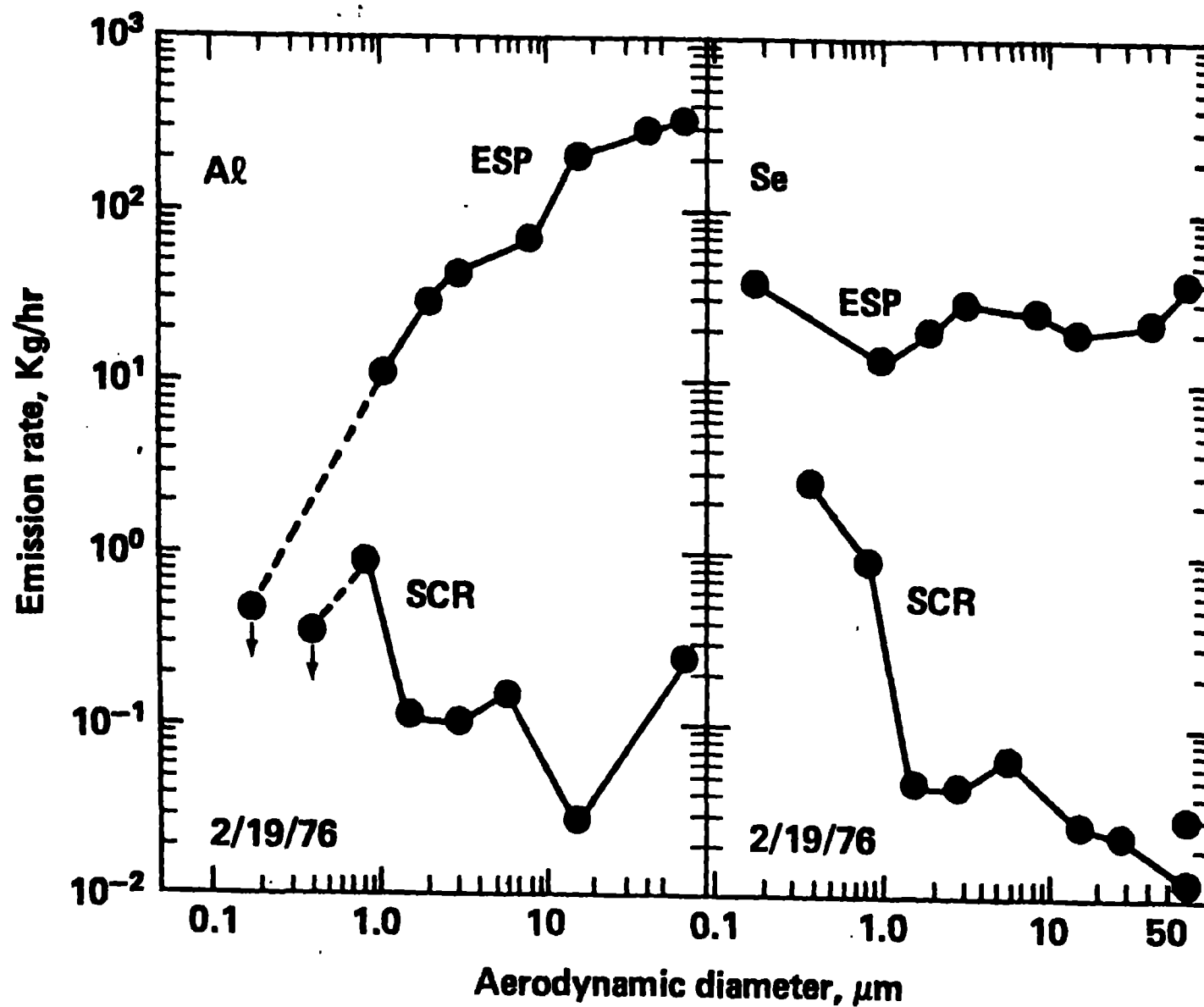


Figure 1

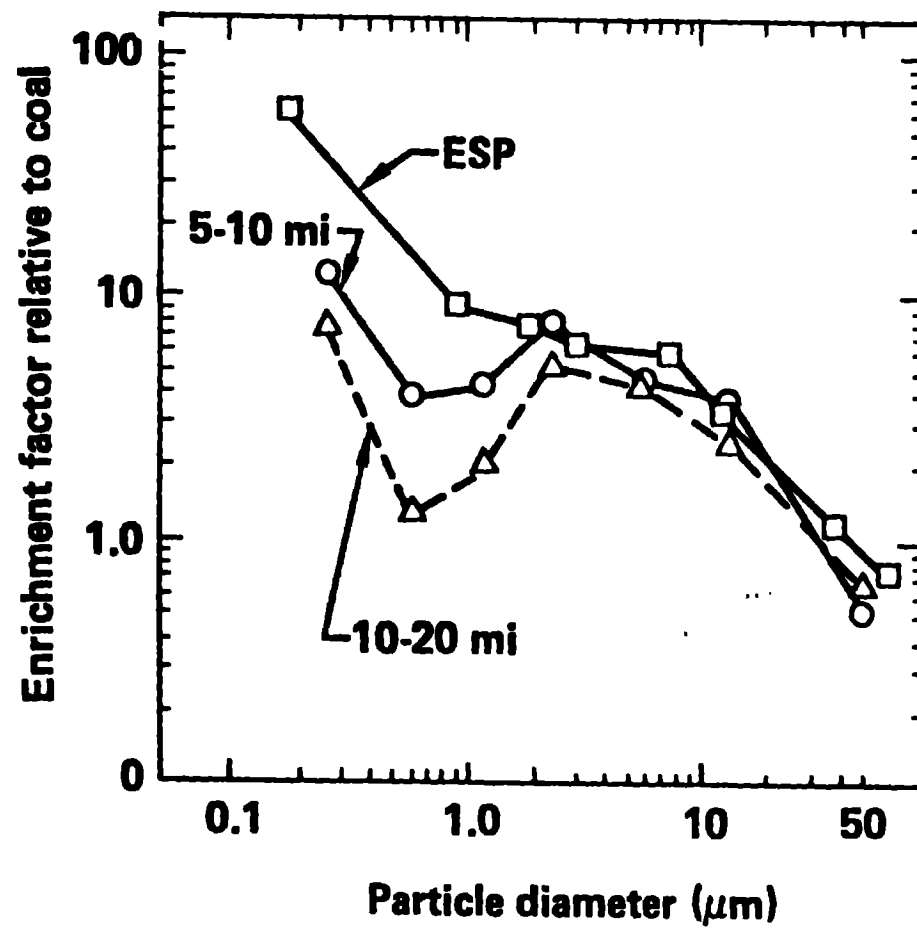
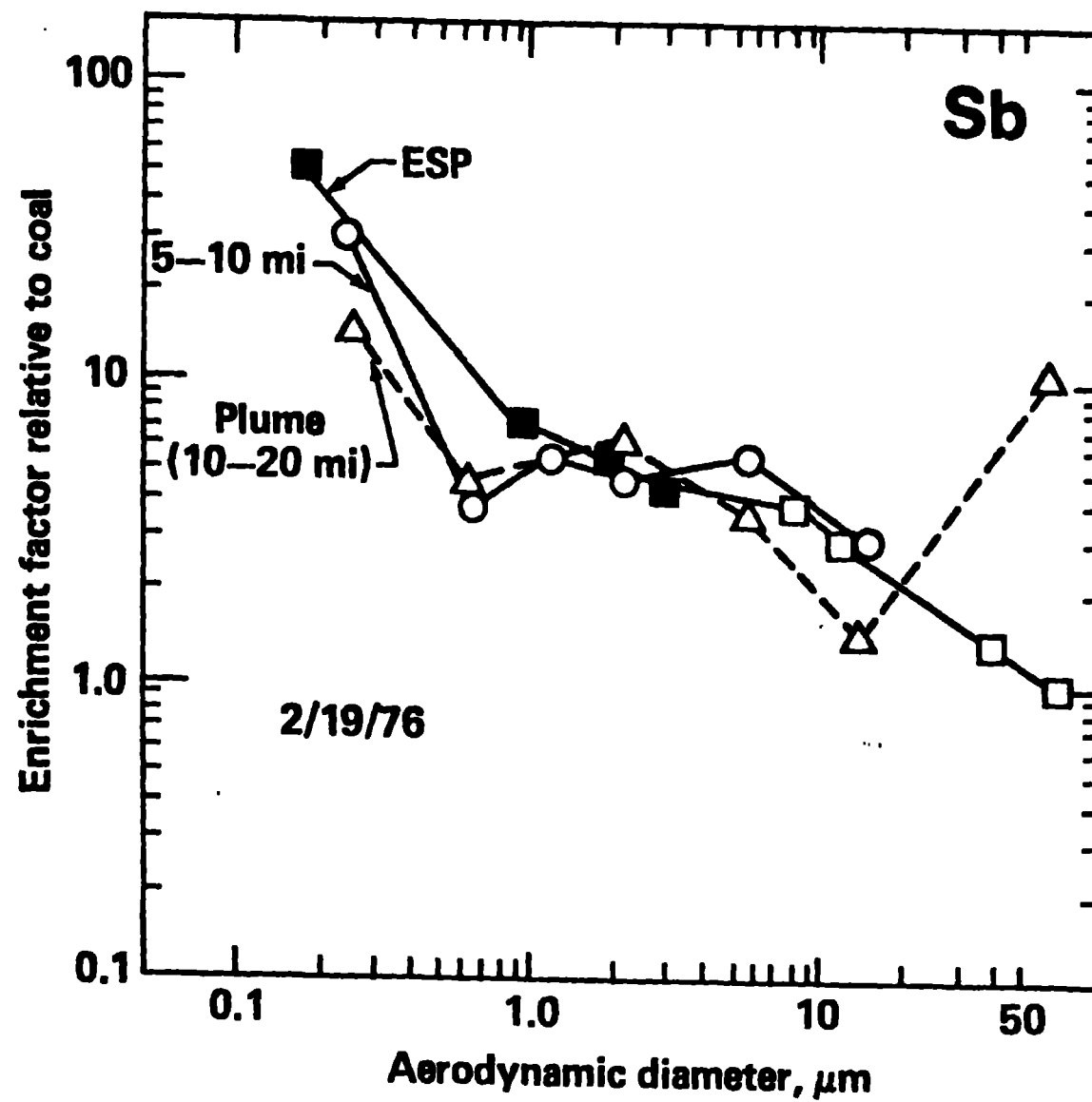
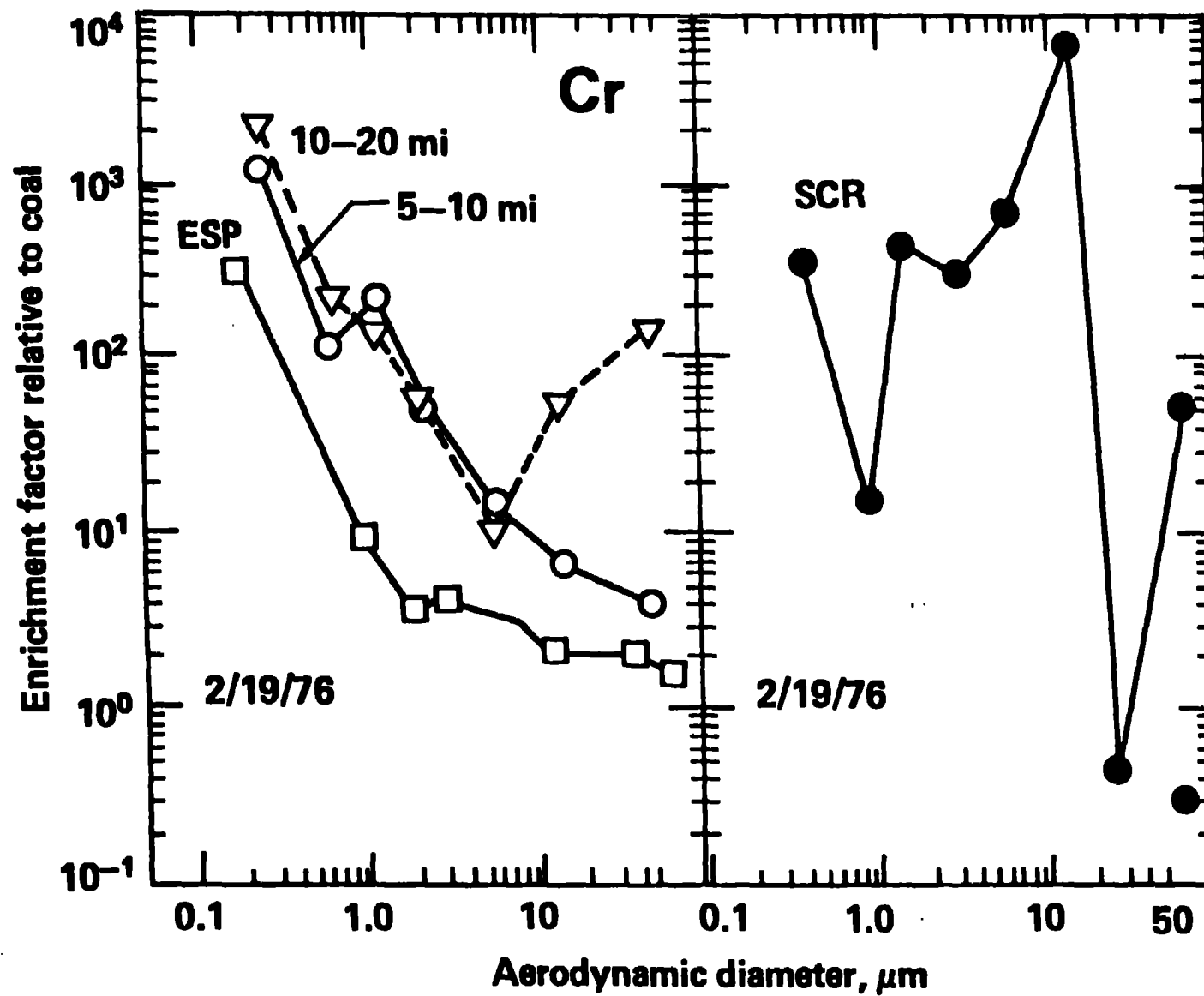


Figure 2







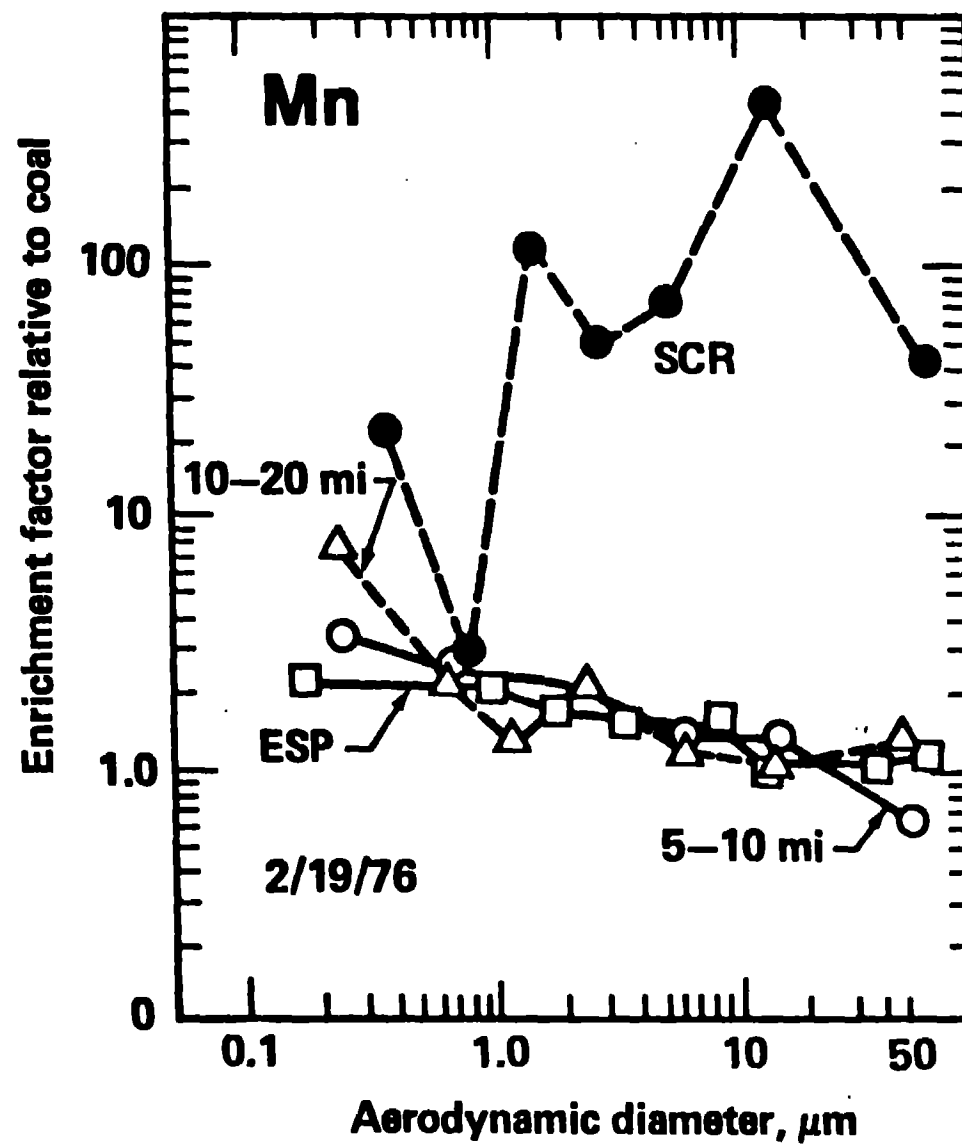


Figure 5